HYDROGEN AND METHANE SOLUBILITY IN SRC-II COAL LIQUID

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INTRODUCTION

The most important steps in coal liquefaction processes are the dissolution of coal in the hydrogen-laden solvent and the subsequent hydrotreating of the coal derived liquid. A small amount of methane is usually formed during coal liquefaction. Thus hydrogen and methane solubility data are essential for the design and operation of coal liquefaction reactors.

A number of investigators studied vapor-liquid equilibrium in binary and multicomponent systems of heavy hydrocarbon liquids and light gases, including hydrogen and methane.(1-11) Only limited experimental data for methane-coal liquid and hydrogen-coal liquid mixtures have been reported in the literature.(5,7) An attempt was made in this study to obtain solubility data in the binary system of hydrogen-coal liquid (SRC-II) and the ternary system of hydrogen-methane-coal liquid (SRC-II) under conditions comparable to those encountered in coal liquefaction processes. Two specially designed in-situ hydrogen probes were adopted for monitoring hydrogen concentration/partial pressure in both vapor and liquid phase.

EXPERIMENTAL

The experimental set-up and procedure used in this study are essentially the same as that described in previous papers.(6, 7) A schematic flow diagram of the equipment is shown in Figure 1.

A one-liter autoclave was used as the equilibrium cell. The autoclave is made of stainless steel and equipped with an automatic temperature controller capable of maintaining constant temperature within ±1 K of the desired setting. A magnatic stirrer, driven by a variable speed motor, was installed in the autoclave. Two in-situ probes were used to measure the hydrogen partial pressure. The operating principle of these probes has been discussed elsewhere.(12)

Hydrogen and methane were supplied to the equilibrium cell from high pressure cylinders through gas feed lines. Liquid and gas samples can be withdrawn from the cell into the low pressure section. A Hewlett-Packard 5880A chromatograph system was used for sample analysis.

High pressure hydrogen (41 MPa) and methane (13 MPa) were used in this work with reported purity of 99.995% and 99.0%, respectively. The SRC-II coal liquid (supplied by the Gulf R&D Co.)(7) was catalytically hydrotreated with Ni-Moly catalyst for four hours at $640^{o}F$.

RESULTS AND DISCUSSION

Hydrogen-Coal Liquid Binary System. The hydrogen solubility data were obtained by measuring hydrogen partial pressure (using the in-situ probe) and by taking liquid samples at temperatures ranging from 420 to 681 K and total pressures from 4 to 11 MPa. Figure 2 shows the hydrogen solubility as a function of total pressure. When the total pressure is held constant, the hydrogen solubility increases with temperature to a maximum value and then decreases. The reason for this apparent solubility inversion is attributable to the rapid increase of coal liquid partial pressure with temperature, which causes a significant decrease in hydrogen partial pressure in the gas phase under constant total pressure. It can be shown that the hydrogen solubility increases monotomously with temperature if hydrogen partial pressure is held constant (Figure 3). In addition, hydrogen solubility data of this study are found to be in good agreement with the results reported by Lin et al[5] at temperatures below 550 K.

Hydrogen-Methane-Coal Liquid Ternary System. Experimental measurements were made at two temperatures, 591 K and 645 K, and at pressures up to 14 MPa. In order to determine the effect of methane on hydrogen solubility, methane partial pressure was varied from zero to 3.5 MPa. The experimental results are plotted in Figures 4 and 5. Under constant hydrogen partial pressure* and temperature, the hydrogen solubilty decreases dramatically with an increase in methane partial pressure. For example, at 645 K and constant hydrogen partial pressure (9.52 MPa), hydrogen concentration in the liquid phase falls from 0.136 to 0.0387 mole fraction when methane partial pressure increases from zero to 3.0 MPa. The methane solubility versus its partial pressure is shown in Figures 6 and 7. The results indicate a linear relationship between methane solubility and its partial pressure at constant temperatures and constant hydrogen partial pressures. A study of the effect of hydrogen partial pressure on methane solubility is underway and the result will be presented in a future paper.

CONCLUSION

Hydrogen and methane solubilities have been experimentally obtained in the binary hydrogen-coal liquid (SRC-II) and ternary hydrogen-methane-coal liquid (SRC-II) systems at elevated temperatures and pressures. In the binary system, hydrogen solubility exhibits a temperature inversion at constant total pressure due to the strong dependence of coal liquid partial pressure on temperature. In the ternary system, hydrogen solubility is affected considerably by methane partial pressure at constant temperatures. The methane solubility exhibits a linear correlation with its partial pressure when hydrogen partial pressure is held constant.

ACKNOWLEDGEMENT

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*The hydrogen partial pressure was accurately measured by the in-situ hydrogen probe.

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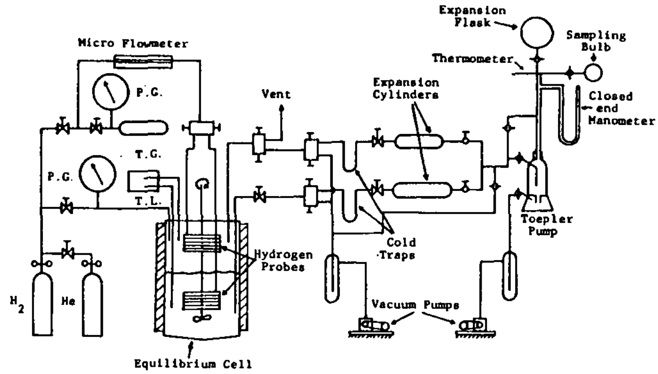

Figure 1 Schematic Diagram of the Experimental Set-up

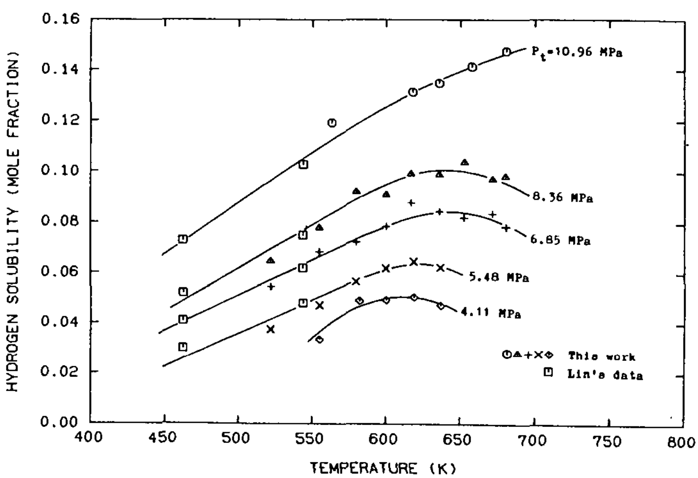

Figure 2 Hydrogen Solubility in SRC-II Coal Liquid vs. Temperature at Constant Total Pressure

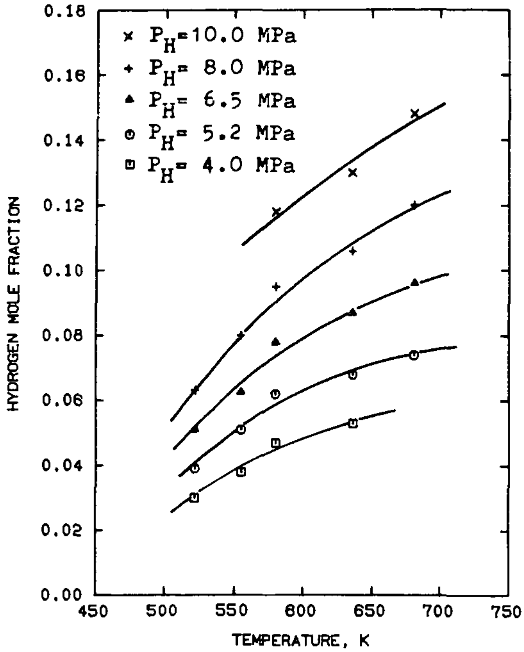

Figure 3 Hydrogen Solubility in SRC-II Coal Liquid vs. Temperature at Constant Hydrogen Partial Pressure

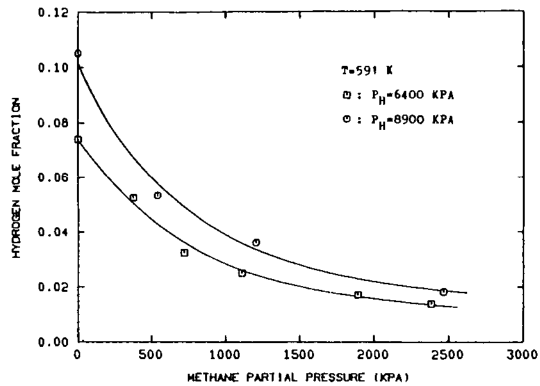

Figure 4 Hydrogen Solubility in SRC-II Coal Liquid vs. Methane Partial Pressure at 591 K

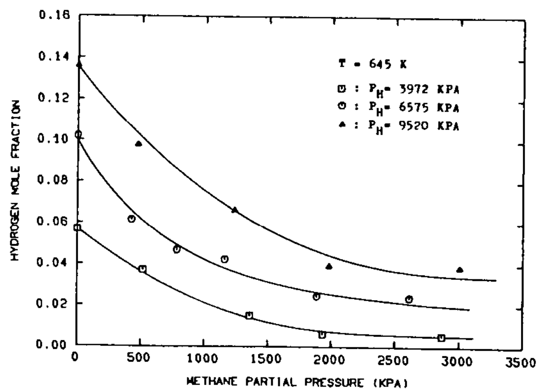

Figure 5 Hydrogen Solubility in SRC-II Coal Liquid vs. Methane Partial Pressure at 645 K

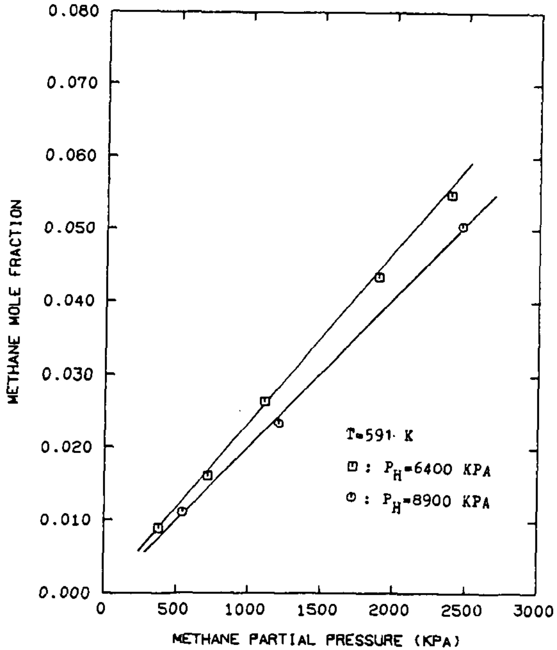

Figure 6 Methane Solubility in SRC-II Coal Liquid vs. Methane Partial Pressure at 591 K

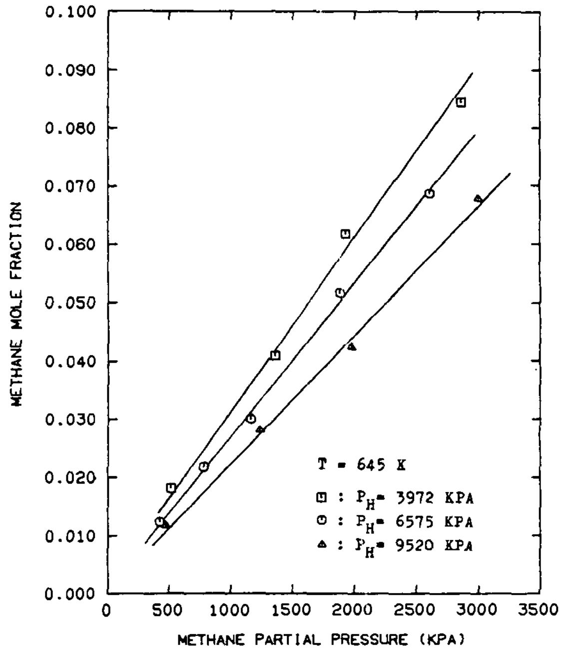

Figure 7 Methane Solubility in SRC-II Coal Liquid vs. Methane Partial Pressure at 645 K